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<b>(54) Title:</b> COMPOSITION AND PROCESS FOR REMOVAL OF ACID GASES  <b>(57) Abstract</b>  Alkanolamines of formula (I): $R-NHCH_2CH(OH)CH_2CH_3$ , or mixtures thereof wherein R is H, $-CH_2CH(OH)CH_2CH_3$ , an alkyl group having from 1 to 6 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms are effective in the removal of acidic gases from a fluid stream containing same and show superior degradation properties as compared to alkanolamines conventionally used in the gas purification applications.		

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COMPOSITION AND PROCESS FOR REMOVAL OF ACID  
GASES

This invention relates to a composition and method  
5 for removing acid gases such as, for example,  $H_2S$ ,  $CO_2$  and  
COS from a fluid stream containing same.

Purification of fluids involves removal of impurities  
from fluid streams. Various fluid purification methods are  
10 known and practiced. These fluid purification methods  
generally fall in one of the following categories:  
absorption into a liquid, adsorption on a solid,  
permeation through a membrane, chemical conversion to  
another compound, and condensation. The absorption  
15 purification method involves the transfer of a component  
of a fluid to a liquid absorbent in which said component  
is soluble. If desired, the liquid containing the  
transferred component is subsequently stripped to  
regenerate the liquid. See, for example, A. Kohl and R.  
20 Nielsen, "Gas Purification", 5<sup>th</sup> edition, Gulf Publishing,  
1997; A. Kohl and F.C. Riesenfeld "Gas Purification", 4<sup>th</sup>  
edition, Gulf Publishing, 1985; A. Kohl and F.C.  
Riesenfeld "Gas Purification", 3rd edition, Gulf  
Publishing, 1979; and "The Gas Conditioning Fact Book"  
25 published by The Dow Chemical of Canada, Limited, 1962;  
all incorporated herein by reference.

Aqueous solutions of various primary, secondary and  
tertiary alkanolamines, such as, for example,  
30 monoethanolamine (MEA), diethanolamine (DEA),  
diglycolamine (DGA), diisopropanolamine (DIPA),  
methyldiethanolamine (MDEA) and triethanolamine (TEA),  
have been used as absorbent liquids to remove acid gases  
from liquid and gas streams. In a regeneration method,  
35 the aqueous alkanolamine solution containing acid gas is  
then subjected to heat to regenerate the aqueous  
alkanolamine solution.

Primary alkanolamines such as MEA and DGA, or secondary alkanolamines such as DEA or DIPA are generally suitable for highly exhaustive removal of CO<sub>2</sub>, however they have disadvantage of requiring large expenditure of energy  
5 for regeneration.

Tertiary alkanolamines, especially MDEA and TEA, require less energy consumption for regeneration, but since they do not react directly with CO<sub>2</sub>, they do not  
10 remove CO<sub>2</sub> completely from the fluid stream. Tertiary alkanolamines are, however, suitable for selective removal of H<sub>2</sub>S from a fluid containing both H<sub>2</sub>S and CO<sub>2</sub>, since the absorption rate for H<sub>2</sub>S is about the same for all alkanolamines.

15

The chemistry of acid gas reactions with aqueous alkanolamine treating solutions is well known and is described in many publications such as, for example, the aforementioned publications and references cited therein,  
20 and publications described below and references cited therein.

Canadian Patent No. 1,091,429 (G. Sartori et al) describes the use of aqueous solutions containing water-  
25 soluble primary monoamines having a secondary carbon atom attached to the amino group in gas purification applications. Primary monoamines having a secondary carbon atom attached to the amino group specifically mentioned in this reference as being suitable are 2-amino-  
30 1-propanol, 2-amino-1-butanol, 2-amino-3-methyl-1-butanol, 2-amino-1-pentanol, 2-amino-1-hexanol and 2-aminocyclohexanol. It is notable that this reference is completely silent as to degradability and corrosivity of these primary monoamines which have a secondary carbon  
35 atom attached to the amino group.

Chem. Eng. Comm., 1996, Vol. 144, pp. 103-112,  
"Effects of Composition on the Performance of Alkanolamine

Blends for Gas Sweetening", describes the influence of blend composition and components on some of the parameters which can be used to monitor the performance of amine blends for aqueous blends of MDEA and MEA, MDEA and DEA, and MDEA and DIPA.

48<sup>th</sup> Annual Laurance Reid Gas Conditioning Conference, March 1-4, 1998, pp. 146-160, "Amine Degradation Chemistry in CO<sub>2</sub> Service", describes the degradation chemistry of various ethanolamines in CO<sub>2</sub> service. The paper promotes gas-treating solvents which are not formulated with primary or secondary ethanolamines as a solution for the loss rates associated with the use of various ethanolamines such as MDEA, MMEA and DEA.

Primary and secondary alkanolamines can also be used as activators in combination with tertiary alkanolamines to remove CO<sub>2</sub> down to as low as 100 parts per million (ppm) or less requiring less regeneration energy than is required using the primary or secondary alkanolamines alone.

U.S. Patent Nos. 5,209,914 and 5,366,709 show how activators such as ethylmonoethanolamine (EMEA) or butylmonoethanolamine (BMEA) can be used with MDEA to achieve better CO<sub>2</sub> removal than MDEA alone.

U.S. Patent No. 4,336,233 discloses that the use of a combination of piperazine and MDEA results in an improved acid gas removal. However, one particular disadvantage of piperazine is that piperazine carbamate formed from the reaction of piperazine and CO<sub>2</sub> is not soluble in the aqueous MDEA/piperazine solution. Thus, the additive level is limited up to about only 0.8 moles/liter, which severely limits the capacity of the solvent, or requires higher circulation rates to treat the same amount of fluid than other MDEA/alkanolamine activator blends require.

The primary disadvantage of using primary and secondary alkanolamines such as MEA, DEA and DIPA is that CO<sub>2</sub> reacts with these alkanolamines to form degradation compounds such as oxazolidinones and ethylenediamines.

5 C. J. Kim, Ind. Eng. Chem. Res. 1988, 27, and references cited therein show how DEA reacts with CO<sub>2</sub> to form 3-(2-hydroxyethyl)-2-oxazolidinone (HEO) and N,N,N'-tris(2-hydroxyethyl)ethylenediamine (THEED). This reference also shows how DIPA reacts to form 3-(2-  
10 hydroxypropyl)-5-methyl-2-oxazolidinone (HPMO). These degradation compounds reduce the amount of alkanolamine available for acid gas removal, increase the viscosity of the solution and potentially increase the corrosivity of the solvent.

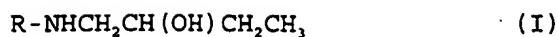
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It is evident that there is still a great need and interest in the gas purification industry for alkanolamine compounds which will be effective in the removal of acidic gases from fluid streams and will have improved  
20 degradation properties compared to alkanolamines commonly used for this purpose.

It has now been discovered that 1-amino-2-butanol and its derivatives are effective in removing acidic gases  
25 from fluid stream and that they have superior degradation properties as compared to alkanolamines conventionally used in the gas purification industry.

In the context of the present invention the term  
30 "fluid stream" encompasses both a gaseous stream and liquid stream.

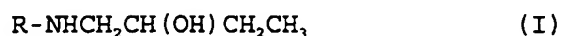
In one aspect the present invention is an aqueous solution adapted for use in the removal of acidic gases  
35 from a fluid stream containing same, said aqueous solution comprising an effective amount of an alkanolamine of the formula



or mixtures thereof wherein R is H,  $-\text{CH}_2\text{CH(OH)CH}_2\text{CH}_3$ , an alkyl group having from 1 to 6 carbon atoms, an aryl group  
5 having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms.

In another aspect the present invention is a process  
10 for removing acidic gases from a fluid stream containing same, said process comprising contacting said fluid stream containing acidic gases with an aqueous solution comprising an effective amount of an alkanolamine of the formula

15



or mixtures thereof wherein R is H,  $-\text{CH}_2\text{CH(OH)CH}_2\text{CH}_3$ , an alkyl group having from 1 to 6 carbon atoms, an aryl group  
20 having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms.

The alkanolamines of the formula I above are  
25 surprisingly found to be effective for removing acidic gases, particularly  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{COS}$  or mixtures thereof, from a fluid stream containing same and yet exhibit much improved degradation properties compared to alkanolamines conventionally used in the gas purification industry.  
30 These compounds are known and their synthesis is described in various publications such as, for example, J. Zienko, M. Stoyanova-Antoszczyszyn and J. Myszkowski, Chemik 1/1991, pp. 8-9, and references cited therein.

35 The alkanolamines of formula I in which R is H,  $-\text{CH}_2\text{CH(OH)CH}_2\text{CH}_3$ , or an alkyl group having from 1 to 6 carbon atoms are preferred in the practice of the present invention with those in which R is H,  $-\text{CH}_2\text{CH(OH)CH}_2\text{CH}_3$ , or

an alkyl group having from 1 to 4 carbon atoms being further preferred. 1-Amino-2-butanol (MBA) and bis(1-hydroxybutyl)-amine (DBA), N-methyl-2-hydroxybutylamine and N-ethyl-2-hydroxybutylamine are particularly preferred, with 1-amino-2-butanol and bis(1-hydroxybutyl)amine (DBA) being the most preferred alkanolamines for use in the present invention.

The alkyl group having from 1 to 6 carbon atoms contemplated by R in formula I can be straight or branched chain alkyl group. Non-limiting examples of such alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, and hexyl.

The aryl group having from 6 to 12 carbon atoms contemplated by R in formula I can be substituted or non-substituted. Non-limiting examples of suitable aryl groups are phenyl and tolyl.

The aralkyl group having from 6 to 12 carbon atoms contemplated by R in formula I can be substituted or unsubstituted. Non-limiting examples of suitable aralkyl groups are benzyl and phenethyl.

The cycloalkyl group having from 3 to 12 carbon atoms contemplated by R in formula I can be substituted or unsubstituted. Non-limiting examples of suitable cycloalkyl groups are cyclohexyl and methylcyclohexyl.

In the present invention, the aqueous solution of an alkanolamine of formula I can be used alone, or in combination with tertiary alkanolamines such as, for example, methyldiethanolamine (MDEA), dimethylethanolamine (DMEA) and triethanolamine (TEA) to remove acidic gases from fluids.



The alkanolamine of formula I is present in the aqueous solution of the present invention in an amount effective to remove acidic gases from a fluid stream.

5        When the alkanolamine of formula I is used alone, it is typically present in an amount of from 7 to 50, preferably from 15 to 40, more preferably from 20 to 30, percent by weight based on the total weight of the aqueous solution.

10

      The optimal amount of the alkanolamine of formula I will depend on the fluid stream composition, outlet fluid requirement, circulation rate, and energy available for stripping the solvent. A person of ordinary skill in the art would readily determine the optimal amount of the

15       alkanolamine of formula I.

      When the alkanolamine of formula I is used as an activator in combination with a tertiary alkanolamine, the amount used can vary quite widely, but it is generally

20       present in an amount of from 1 to 30, preferably from 5 to 20, more preferably from 7 to 15, percent by weight based on the total weight of the aqueous solution. The tertiary alkanolamine is generally used in an amount of from 25 to

25       60, preferably from 25 to 40, more preferably from 30 to 40, percent by weight based on the total weight of the aqueous solution.

      The process of the present invention can be carried

30       out in any conventional equipment for the removal of acidic gases from fluids and detailed procedures are well known to a person of ordinary skill in the art. See, for example, U.S. Patent No. 1,783,901 (Bottoms) and subsequent improvements which are known in the art.

35

      The process according to the present invention can be conveniently carried out in any suitable absorber. The great number of absorbers used for gas purification

operations include packed, plate, or spray towers. These absorbers are interchangeable to a considerable extent although certain specific conditions may favor one over the other. In addition to conventional packed, plate, or spray towers, specialized absorber towers have been developed to meet specific process requirements. Examples of these specific towers include impingement-plate scrubbers and turbulent contact scrubbers. The process of the present invention can be carried out in either packed, plate, or spray towers, and can contain other peripheral equipment as necessary for optimal process operation. Such peripheral equipment may include an inlet gas separator, a treated gas coalescor, a solvent flash tank, a particulate filter and a carbon bed purifier. The inlet gas flow rate vary depending on the size of the equipment but is typically between 5 and 100 million standard cubic feet per day (SCFD). The solvent circulation rate will depend on the amine concentration, the gas flow rate, gas composition, total pressure and treated fluid specification. The solvent circulation rate is typically between 5 and 5000 gallons per minute (gpm). Pressure inside the absorber can vary between 0 and 1200 psig depending on the type of fluid being processed.

The absorbers, strippers and peripheral equipment useful for carrying out the process of the present invention are well known in the art and are described in many publications including the aforementioned references.

In the process of the present invention, a fluid containing an acid gas is contacted with an aqueous solution comprising an effective amount of an alkanolamine of formula I at a temperature of from ambient temperature (approximately 25°C, 77°F) up to 93°C (200°F).

Temperatures inside the stripper tower, if one is employed, can vary between 82°C (180°F) and 127°C (260°F). The stripper overhead pressure is typically between 0 and

20 psig. Optionally, corrosion inhibitors, scale inhibitors and antifoam agents may be employed.

The following examples are offered to illustrate but not limit the invention. Percentages, ratios and parts are by weight unless stated otherwise.

EXAMPLES 1 TO 3 AND COMPARATIVE EXAMPLES C-1 TO C-3

Dissolved CO<sub>2</sub> experiments were performed by sparging the compressed CO<sub>2</sub> (Liquid Carbonic HI-DRY Grade; greater than 99.99 percent purity) through a Cole-Palmer 0-150 ml/min. flowmeter at a rate of 50 ml/min. for 90 min. into an aqueous solution (200 ml) comprising MDEA (2.94 mole; 35 percent) and an additive (1.68 mole) contained in a 250 ml jacketed beaker. The aqueous solution was stirred with a magnetic stir bar while continually sparging with CO<sub>2</sub>. The temperature of the solution (31°C) was adjusted using a GCA Precision R10 circulating bath and was monitored using a thermometer. A polycarbonate cover with slits for the thermometer, gas entrance and exit was used on top of the beaker to prevent CO<sub>2</sub> in the atmosphere from entering the solution. After 90 minutes of continuous sparging, the solution was analyzed for dissolved CO<sub>2</sub> according to ASTM Method No. D 513 "Total and Dissolved CO<sub>2</sub> in Water". The additives used and results obtained are given in Table 1 below.

Table 1  
CO<sub>2</sub> Reaction with MDEA/Additive

Example	Aqueous Solution	Wt % CO <sub>2</sub> Absorbed in 90 minutes
1	MDEA + MBA (Run 1)	4.25
2	MDEA + MBA (Run 2)	4.01
3	MDEA + DBA	3.76
C-1	MDEA + MEA	4.16
C-2	MDEA + DEA	3.76

C-3	MDEA + 1.68M EMEA	3.71
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This data shows that the aqueous solutions containing MBA absorbed more CO<sub>2</sub> than those containing DEA or EMEA. The amount of CO<sub>2</sub> absorbed by the solutions containing MBA (average: 4.13 percent by weight) is statistically similar to the amount of CO<sub>2</sub> absorbed by the solution containing MEA (4.16 percent by weight). Likewise, the amount of CO<sub>2</sub> absorbed by the aqueous solution containing DBA is also statistically similar to amount of CO<sub>2</sub> absorbed by the aqueous solutions containing DEA or EMEA.

EXAMPLES 4 and 5 AND COMPARATIVE EXAMPLES C-4 and C-5

Autoclave degradation tests were performed on equimolar amine solutions using 0.050 mole of CO<sub>2</sub> per mole of amine at 126.7°C (260°F). An aqueous solution (1100 ml.) containing MDEA (35 percent by weight; 2.94 mole) and either EMEA (15 percent by weight; 1.68 mole), DEA (17.7 percent by weight; 1.68 mole) or MBA (15 percent by weight; 1.68 mole) was added to a 2 liter Parr autoclave. Then each solution was loaded with CO<sub>2</sub> such that the CO<sub>2</sub> loading was 0.050 mole of CO<sub>2</sub> per mole of total amine. The solution was then heated for 28 days at 126.7°C (260°F). After 28 days, the solutions were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) to determine the amount of the amine additive remaining in the solution and for the presence of degradation/conversion products. The results obtained are given in Table 2 below.

Table 2  
Degradation Tests

Example	Aqueous Solution	Amine Additive Remaining after 28 Days	Degradation / Conversion Product
4	MDEA + MBA (Run 1)	15.1 wt%	none

5	MDEA + MBA (Run 2)	14.99 wt%	none
C-4	MDEA + EMEA	10.6 wt%	yes (3 wt%)
C-5	MDEA + DEA	9.39 wt%	yes (2.2 wt%)

This data clearly shows the unexpected advantage of MBA over EMEA and DEA. The data demonstrates that substantially all of MBA remains in the solution after 28 days with no detection of any degradation product while during the same time substantial amount of EMEA and DEA has been lost due to their reactivity with CO<sub>2</sub> and conversion into undesirable reaction products.

EXAMPLES 6 AND 7 AND COMPARATIVE EXAMPLES C-6 AND C-7

Autoclave degradation tests were performed on equimolar amine solutions using 0.050 mole of CO<sub>2</sub> per mole of amine at 126.7°C (260°F). An aqueous solution (1100 ml.) containing MDEA (35 percent by weight) and either EMEA (15 percent by weight), BMEA (15 percent by weight), MBA (15 percent by weight), or DBA (15 percent by weight) was added to a 2 liter Parr autoclave. Then each solution was loaded with CO<sub>2</sub> such that the CO<sub>2</sub> loading was 0.050 mole of CO<sub>2</sub> per mole of total amine. The solution was then heated for 28 days at 126.7°C (260°F). After 28 days, the solutions were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) to determine the amount of the amine additive remaining in the solution and for the presence of degradation/conversion products. The amount of EMEA, BMEA, MBA (two runs) and DBA remaining in the solution after 28 days was 10.6, 10.4, 15.1, 14.99 and 12.3 weight percent, respectively. EMEA converted to 3 weight percent of N,N'-(2-hydroxyethyl)ethylene-diamine. BMEA converted to 3.2 weight percent of N,N'-dibutyl-N-(2-hydroxyethyl)ethylenediamine plus a small amount (less than 0.5 weight percent) of N-butyl-2-oxazolidinone. MBA showed very little degradation. Less than 0.2 weight percent what is possibly an oxazolidinone or substituted ethylenediamine was detected by GC and GC/MS. DBA converted to 2.9 weight percent of a product that is preliminary identified as N-(2-hydroxy-butyl)-2-oxazolidinone by GC/MS analysis. The results are given in Table 3 below.

Table 3  
Degradation Tests

Example	Aqueous Solution	Amine Additive Remaining after 28 Days	Degradation / Conversion Product
6	MDEA + MBA (Run 1)	15.1 wt%	Yes (<0.2 wt%)
7	MDEA + MBA (Run 2)	14.99 wt%	Yes (<0.2 wt%)
8	MDEA + DBA	12.3 wt%	Yes (2.9 wt%)
C-6	MDEA + EMEA	10.6 wt%	Yes (3 wt%)
C-7	MDEA + DEA	9.39 wt%	Yes (3.7 wt%)

5           This data also shows the unexpected advantage of MBA  
and DBA over EMEA and BMEA. The data demonstrates that  
substantially all of MBA remains in the solution after 28  
days with essentially no detection of any degradation  
product while during the same time substantial amount of  
10 EMEA and DEA has been lost due to their reactivity with CO<sub>2</sub>  
and conversion into undesirable reaction products.

EXAMPLE 9 AND COMPARATIVE EXAMPLE C-8

15           Autoclave degradation tests were performed on 2.80  
mole amine solutions using 0.050 mole of CO<sub>2</sub> per mole of  
amine at 126.7°C (260°F). An aqueous solution (1100 ml.)  
containing MEA (17.7 percent by weight, 2.80 mole) or MBA  
(25 percent by weight, 2.80 mole) was added to a 2 liter  
20 Parr autoclave. Then each solution was loaded with CO<sub>2</sub>  
such that the CO<sub>2</sub> loading was 0.050 mole of CO<sub>2</sub> per mole of  
total amine. The solution was then heated for 28 days at  
126.7°C (260°F). After 28 days, the solutions were  
analyzed by gas chromatography (GC) and gas  
25 chromatography/mass spectrometry (GC/MS) to determine the  
amount of the amine additive remaining in the solution and  
for the presence of degradation/conversion products. The  
amount of MEA and MBA remaining in the solution after 28  
days was 16.47 and 24.71 weight percent, respectively. GC  
30 and GC/MS did not positively identify any of small

degradation peaks for either MEA or MBA runs. The results are given in Table 4 below.

Table 4  
Degradation Tests

5

Example	Aqueous Solution	Amine Additive Remaining after 28 Days	Degradation
9	MBA	24.71 wt%	1.2 wt%
C-8	MEA	16.47 wt%	6.9 wt%



## WHAT IS CLAIMED IS:

1. An aqueous solution adapted for use in the removal of acidic gases from a fluid stream containing  
5 same, said aqueous solution comprising an effective amount of an alkanolamine of the formula



- 10 or mixtures thereof wherein R is H,  $-\text{CH}_2\text{CH(OH)CH}_2\text{CH}_3$ , an alkyl group having from 1 to 6 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms.

15

2. The aqueous solution according to Claim 1 wherein the alkanolamine of formula I is present in an amount of from 7 to 50 percent by weight.

- 20 3. The aqueous solution according to Claim 1 further comprising a tertiary alkanolamine.

4. The aqueous solution of Claim 3 wherein the alkanolamine of formula I is present in an amount of from  
25 1 to 30 percent and the tertiary alkanolamine is present in an amount of from 25 to 60 percent.

5. The aqueous solution according to Claim 3 wherein the tertiary alkanolamine is selected from the  
30 group consisting of methyldiethanolamine, dimethylethanolamine and triethanolamine.

6. The aqueous solution according to Claim 1 or Claim 3 wherein R in formula I is H,  $-\text{CH}_2\text{CH(OH)CH}_2\text{CH}_3$ ,  
35 or an alkyl group having from 1 to 6 carbon atoms.

7. The aqueous solution according to Claim 1 or Claim 35 wherein the alkanolamine of formula I is

selected from the group consisting of 1-amino-2-butanol, bis(1-hydroxybutyl)amine, N-methyl-2-hydroxybutylamine and N-ethyl-2-hydroxybutylamine.

5           8. The aqueous solution according to Claim 7 wherein the alkanolamine of formula I is present in an amount of from 1 to 30 percent by weight and further containing methyldiethanolamine in an amount of from 25 to 60 percent by weight.

10

          9. The aqueous solution according to Claim 7 wherein the alkanolamine of formula I is a mixture of 1-amino-2-butanol and bis(1-hydroxybutyl)amine.

15

          10. A process for removing acidic gases from a fluid stream containing same, said process comprising contacting said fluid stream with an aqueous solution comprising an effective amount of an alkanolamine of the formula

20



or mixtures thereof wherein R is H,  $-\text{CH}_2\text{CH(OH)CH}_2\text{CH}_3$ , an alkyl group having from 1 to 6 carbon atoms, an aryl group  
25 having from 6 to 12 carbon atoms, an aralkyl group having from 6 to 12 carbon atoms, or a cycloalkyl group having from 3 to 6 carbon atoms.

          11. The process according to Claim 10 wherein  
30 the alkanolamine of formula I is present in an amount of from 7 to 50 percent by weight.

          12. The process according to Claim 10 wherein the aqueous solution further comprises a tertiary  
35 alkanolamine.

          13. The process according to Claim 12 wherein the alkanolamine of formula I is present in an amount of

from 1 to 30 percent and the tertiary alkanolamine is present in an amount of from 25 to 60 percent.

14. The process according to Claim 12 wherein  
5 the tertiary alkanolamine is selected from the group consisting of methyldiethanolamine, dimethylethanolamine and triethanolamine.

15. The process according to Claim 10 or Claim  
10 12 wherein R in formula I is H,  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ , or an alkyl group having from 1 to 6 carbon atoms.

16. The process according to Claim 10 or Claim  
12 wherein the alkanolamine of formula I is selected from  
15 the group consisting of 1-amino-2-butanol, bis(1-hydroxybutyl)amine, N-methyl-2-hydroxybutylamine and N-ethyl-2-hydroxybutylamine.

17. The process according to Claim 16 wherein  
20 the alkanolamine of formula I is present in an amount of from 1 to 30 percent by weight and the solution further contains methyldiethanolamine in an amount of from 25 to 60 percent by weight.

25 18. The process according to Claim 16 wherein the alkanolamine of formula I is a mixture of 1-amino-2-butanol and bis(1-hydroxybutyl)amine.

# INTERNATIONAL SEARCH REPORT

Int. National Application No.

PCT/US 99/20256

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B01D53/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 647 462 A (KANSAI ELECTRIC POWER CO ;MITSUBISHI HEAVY IND LTD (JP)) 12 April 1995 (1995-04-12) page 4, line 27 - line 36 page 4, line 43 - line 44 page 4, line 48 - line 51 page 4, line 56 -page 5, line 7	1-6, 10-15
A	NL 7 800 153 A (EXXON RESEARCH ENGINEERING CO) 10 July 1978 (1978-07-10) claims 1-8 & CA 1 091 429 A cited in the application	7-9, 16-18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

21 December 1999

Date of mailing of the international search report

11/01/2000

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/20256

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0647462 A	12-04-1995	JP 2871422 B	17-03-1999
		JP 7100334 A	18-04-1995
		JP 2871447 B	17-03-1999
		JP 7246314 A	26-09-1995
		CN 1110624 A	25-10-1995
		EP 0875280 A	04-11-1998
		US 5700437 A	23-12-1997
NL 7800153 A	10-07-1978	CA 1091429 A	16-12-1980